

## Effect of humic acid contact time on the diffusion of Re(VII) in GMZ bentonite\*

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The effect of humic acid (HA) on the diffusion of Re(VII) was investigated in compacted Gaomiaozi (GMZ) bentonite by the through- and out- diffusion method. The effective diffusion coefficient,  $D_e$ , and accessible porosity,  $\epsilon_{acc}$ , were measured in order to evaluate the impact of humic acid on Re(VII) diffusion. The  $D_e$  value was in the range of  $(5.2-8.3) \times 10^{-12} \text{ m}^2/\text{s}$ . The diffusion of Re(VII) was enhanced in the presence of HA, and the  $D_e$  value increased with the increase of ageing time, indicating that the formation of HA-Re complexes was slow. Moreover, the  $\epsilon_{acc}$  was in the range of (0.06–0.16), which is less than the total porosity. It implies that the HA-Re complexes are anions.

Keywords: Diffusion coefficient, Humic acid, Re(VII), Complex, Bentonite

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## I. INTRODUCTION

Humic acids (HA) possess a strong ability for metal complexation. They can alter the migration of radionuclides in clay environments. Several studies have shown that some radionuclides are strongly retained in humics-rich surface soils [1, 2]. For example, the migration of Eu(III) in bentonite is hindered by HA because of the formation of the Eu-HA complexes at the surface of compacted bentonite [1]. In addition, the diffusion of Cu(II) is prevented by humic gels and the diffusion coefficient in the presence of humic gels is two orders of magnitude lower than that in water [2]. However, humics also facilitate radionuclide transport by the formation of radionuclides-colloid complexes. Wold *et al.* [3] found that humics could make the apparent diffusion coefficient  $D_a$  increase and the distribution coefficient,  $K_d$ , values decrease for both Co(II) and Eu(III) in compacted bentonite.

<sup>99</sup>Tc is a significant environmental contaminant with a long half-life of  $2.1 \times 10^5$  years. <sup>99</sup>Tc presents a challenge for clean up because it is difficult to understand the key processes that affect its mobility in the environment. Tc(VII) is the most stable in natural oxic environments and it has high solubility in water and essentially no absorptive properties toward minerals. As contrasted with Tc(VII), Tc(IV) is less soluble and can be immobile in underground water and soils [4–6].

Several researchers have focused on the effect of humic substances (HS) on Tc(IV) mobility [7–9]. For instance, Artinger *et al.* [7] show that humic substances (HS) enhanced the mobility of Tc(IV) to form the soluble Tc(IV)-HS species. Boggs *et al.* [9] found that TcO(OH)-HA was the predominant complex under acidic conditions, whereas TcO(OH)<sub>2</sub><sup>0</sup>

and TcO(OH)<sub>2</sub>-HA were the major species under neutral and alkaline conditions, respectively. XANES and EXAFS measurements show that the soluble Tc(IV)-HS species are formed in terms of ligand-metal complexation under slightly basic pH and reducing conditions [10]. Moreover, Maes *et al.* [11] explained the transport of Tc(IV) with organic matter as an organic matter complex/colloid that slowly dissociates. Studies also show that organic ligand like oxalate and acetate increase Tc(IV) solubility [4, 12]. Even in the case of Tc(VII), Maes *et al.* [13] found that Tc(VII) was reduced to Tc(IV) by the solid Boom clay phase, then the competition effect for Tc(IV) was described between the solid phase and dissolved HS.

In the safety assessment of high level radioactive waste repository, the radionuclide species with high mobility, such as <sup>99</sup>TcO<sub>4</sub><sup>−</sup>, <sup>125</sup>I<sup>−</sup>, <sup>36</sup>Cl<sup>−</sup>, and <sup>79</sup>SeO<sub>3</sub><sup>2−</sup>, are given the most concerned in the pre-safety assessment [14–17]. The bentonite in Gaomiaozi county China (GMZ bentonite) has been selected as the backfill material for the high level radioactive waste repository. The effective/apparent diffusion coefficient,  $D_e/D_a$ , porosity,  $\epsilon_{tot}$  and distribution coefficient,  $K_d$ , are the fundamental parameters in modeling the radionuclide transport behaviors for a safety assessment of the repository.

Our recent work showed that EDTA can enhance TcO<sub>4</sub><sup>−</sup> transport, but not alter the mobility of ReO<sub>4</sub><sup>−</sup> (as analogue to <sup>99</sup>TcO<sub>4</sub><sup>−</sup>) due to less reactivity of ReO<sub>4</sub><sup>−</sup> [18]. In addition, Liu *et al.* [19] found that HA has insignificant effect on the diffusion of Tc(VII) in granite. However, the investigations were performed without consideration of the effect of aging time of HA. The difference might be overlapped by the uncertainty or other unknown factors. In this work, the effect of HA on the diffusion of ReO<sub>4</sub><sup>−</sup> is under different aging time conditions. The  $D_e$  and accessible porosity ( $\epsilon_{acc}$ ) were obtained by fitting the experimental data of both the transient and steady states. Out-diffusion method was employed to clarify if the interaction between ReO<sub>4</sub><sup>−</sup> and HA reached equilibrium.

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## II. MATERIALS AND METHODS

### A. Material and experimental conditions

The experiments were carried out by through- and out-diffusion methods. Table 1 shows the experimental conditions for the diffusion experiments.

The GMZ bentonite was obtained from the Beijing Research Institute of Uranium Geology without further processing.  $\text{ReO}_4^-$  was prepared in distilled water using  $\text{NH}_4\text{ReO}_4$  (Alfa Aesar, 99.997%). HA (Sigma-Aldrich) was dissolved by adding a small amount of 0.01 mol/L NaOH.

TABLE 1. Experimental conditions for diffusion experiments

Item	Condition/method
Method	Through- and out-diffusion methods
Bentonite dry density ( $\text{kg/m}^3$ )	GMZ (75.4 wt.% montmorillonite) 1800
Temperature ( $^\circ\text{C}$ )	$20 \pm 5$
Atmosphere	ambient condition
Saturated solution	artificial pore water of Gansu Beishan (pH 7.6)
Humic acid ( $\text{mg/L}$ )	10
pH of tracer solution	2.5 – 3

### B. Data processing

For the through-diffusion, the diffusion parameters  $D_e$  and  $\alpha$  were obtained by fitting the following equations

$$A_{\text{cum}} = SLC_0 \left( \frac{D_e t}{L^2} - \frac{\alpha}{6} - \frac{2\alpha}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp \left\{ -\frac{D_e n^2 \pi^2 t}{L^2 \alpha} \right\} \right), \quad (1)$$

based on the following initial and boundary conditions:

$$\begin{aligned} c(x, t) &= 0, & t &= 0; & \forall x, \\ c(0, t) &= C_0, & x &= 0; & t > 0, \\ c(L, t) &= 0, & x &= L; & t > 0, \end{aligned}$$

where  $L$  (m) is the sample thickness;  $C_0$  ( $\mu\text{g/m}^3$ ) is the initial concentration of the diffusing species;  $A_{\text{cum}}$  ( $\mu\text{g}$ ) is the total amount of diffused species through a boundary at  $x = L$  and at diffusion time  $t$ ;  $S$  ( $\text{m}^2$ ) is the cross section area of the clay.

The equations of out-diffusion can be described as follows:

$$J(0, t) = 2J_L \sum_{n=1}^{\infty} e^{-\left(\frac{n\pi}{L} \frac{D_e}{\alpha} t\right)} \quad \text{at } x = 0, \quad (2)$$

$$J(L, t) = 2J_L \sum_{n=1}^{\infty} (-1)^n e^{-\left(\frac{n\pi}{L} \frac{D_e}{\alpha} t\right)} \quad \text{at } x = L, \quad (3)$$

where  $J(0, t)$  and  $J(L, t)$  are fluxes at the high and low concentration boundaries, respectively.

The experimental procedure was consistent with the literature [14, 18, 20]. The equilibrium condition is that the artificial pore water containing 10 mg/L humic acid is in contact with bentonite for 5 weeks. Aging conditions were that 10 mg/L humic acid mixed with  $\text{ReO}_4^-$  in artificial pore water was aged for 0 and 60 days, respectively. The source reservoir was spiked with (0.6–1.6) g/L  $\text{ReO}_4^-$ . The solutions in the target reservoirs were replaced to keep the concentration of  $\text{ReO}_4^-$  in this reservoir as low as possible. After finishing the through- diffusion experiment, a 10 mL solution without  $\text{ReO}_4^-$  and HA in both reservoirs was replaced and the out-diffusion experiment was started. The sample was determined by ICP-OES (PerkinElmer Optima 2100D-V). The experimental and theoretical data processing of the through- and out- diffusion methods have been described previously [14, 21, 22].

The composition of the GMZ bentonite samples were analyzed by the powder X-ray diffraction (XRD) with a Model XD-2 (Beijing Purkinje General Instrument Co., Ltd., China) using CuK (radiation at 35 kV/20 mA). The morphology and structure of bentonite were observed using a scanning electron microscope (Hitachi S-3400N).

## III. RESULTS AND DISCUSSION

Constituent mineral composition of bentonite could be detected through X-ray diffraction. Fig. 1(a) shows scanning electron microscopy (SEM) images of GMZ bentonite. The most composition was montmorillonite with a characteristic peak at  $2\theta = 6.14^\circ, 19.9^\circ, 36.7^\circ$  and  $55.4^\circ$ . Other minerals, such as feldspars, quartz, and  $\text{Ca-Fe(Ca)CO}_3$ , were also present in GMZ bentonite. The layer structure of GMZ bentonite consisted of one alumina octahedral sheet located between the two silica tetrahedral sheets. The same result can be found in other GMZ [23, 24] and MX-80 [25] bentonite research. The results of the analysis by scanning electron microscopy show (Fig. 1(b)) that GMZ bentonite has a multi-layer structure and smoothed shapes.

Figure 2 shows the  $A_{\text{cum}}$  (2(a)) and Flux (2(b)) vs. time for  $\text{ReO}_4^-$  in HA equilibrium, HA aging 0 days and aging 60 days 3 kinds of condition at  $1800 \text{ kg/m}^3$  compacted GMZ bentonite by through-diffusion method.

Through- diffusion experiments of  $\text{ReO}_4^-$  in the presence of different HA conditions (HA equilibrium, HA aging 0 days and aging 60 days) were studied by compacting GMZ bentonite at  $1800 \text{ kg/m}^3$ , respectively. Fig. 2 shows the  $A_{\text{cum}}$  and flux as a function of diffusion time. Diffusion parameters are listed in Table 2. It shows a typical diffusion curve. The flux increased dramatically at the transient phase, then remains unchanged at the steady phase. The  $D_e$  and rock capacity factor  $\alpha$  values were obtained from the steady and transient phases, respectively.  $\alpha$  is equal to the accessible porosity  $\epsilon_{\text{acc}}$  for anions [20]. The time to reach the steady phase was 5, 8 and 12 days under equilibrium, aging 0 and 60-day conditions. The breakthrough curves of flux were almost identical

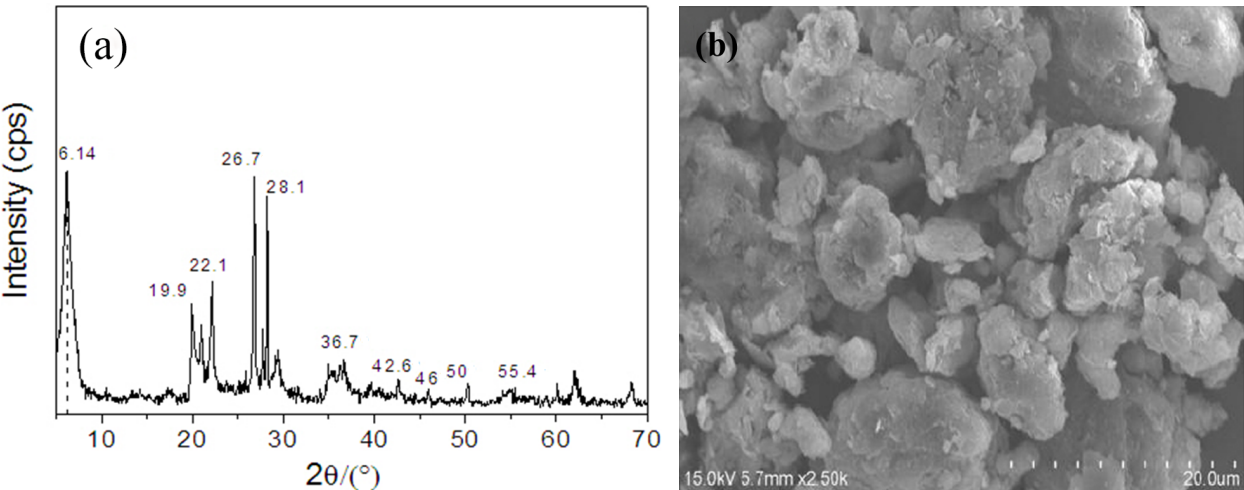


Fig. 1. XRD pattern (a) and SEM photograph (b) of GMZ bentonite

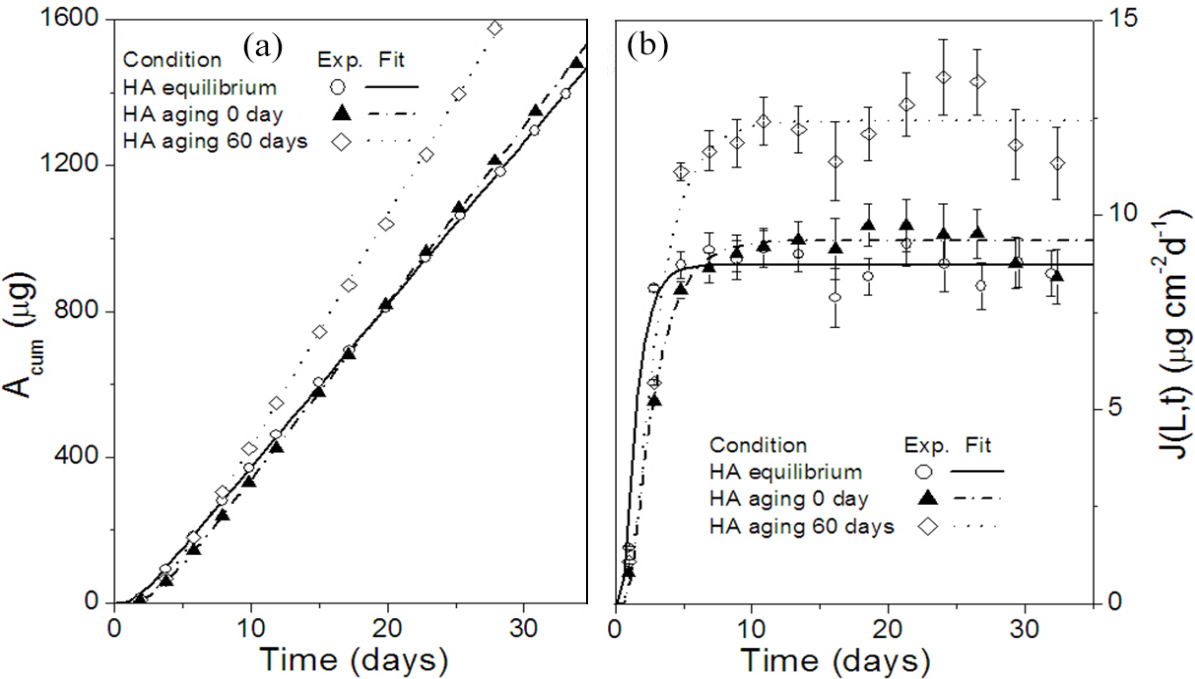


Fig. 2.  $A_{cum}$  (a) and Flux (b) vs. time for  $ReO_4^-$  in three kinds of condition, namely HA equilibrium, HA aging 0 and aging 60 days, at  $1800\text{ kg/m}^3$  compacted GMZ bentonite by through-diffusion method.

TABLE 2. Diffusion parameters for  $ReO_4^-$  in compacted GMZ bentonite

Sample	Condition	$C_0$ (mg/L)	$D_e$ ( $\times 10^{-11}\text{ m}^2/\text{s}$ )	$D_a$ ( $\times 10^{-11}\text{ m}^2/\text{s}$ )	$\epsilon_{acc}$
Re(VII)	HA equilibrium	$1600 \pm 50$	$0.52 \pm 0.05$	$8.67 \pm 2.28$	$0.06 \pm 0.01$
	HA aging 0 day	$1600 \pm 50$	$0.59 \pm 0.03$	$4.92 \pm 3.12$	$0.12 \pm 0.07$
	HA aging 60 days	$1600 \pm 50$	$0.83 \pm 0.09$	$5.19 \pm 1.12$	$0.16 \pm 0.02$

under equilibrium and aging 0 conditions. Since humic substances can absorb on silica sheets of montmorillonite in lower pH [26] and clogged bentonite pore space [27], it implies that the interaction between HA and Re(VII) is stronger than

that of between HA and bentonite. Therefore, Re(VII)-HA complexes can be formed. Moreover, the flux under aging 60-day condition was higher than the others, indicating that the formation of Re(VII)-HA complexes was slow. Fig. 1(b)

verified the breakthrough curves of flux, that is, the  $A_{\text{cum}}$  was almost identical under equilibrium and aging 0 conditions and it increased fastest under aging 60-day conditions.

Table 2 shows the measured diffusion parameters for  $\text{ReO}_4^-$  in GMZ bentonite. The apparent diffusion coefficient ( $D_a$ ) is calculated as follows:

$$D_a = \frac{D_e}{\alpha}. \quad (4)$$

The  $D_e$  value under aging 60-day condition was higher than that of under equilibrium and aging 0 day conditions. It demonstrates that HA can enhance the mobility of  $\text{Re(VII)}$ . The  $\varepsilon_{\text{acc}}$  values were less than the total porosity  $\varepsilon$  values, which is measured by the HTO through-diffusion method in GMZ bentonite [22]. It indicates that the  $\text{Re(VII)}$ -HA complexes are anionic species.

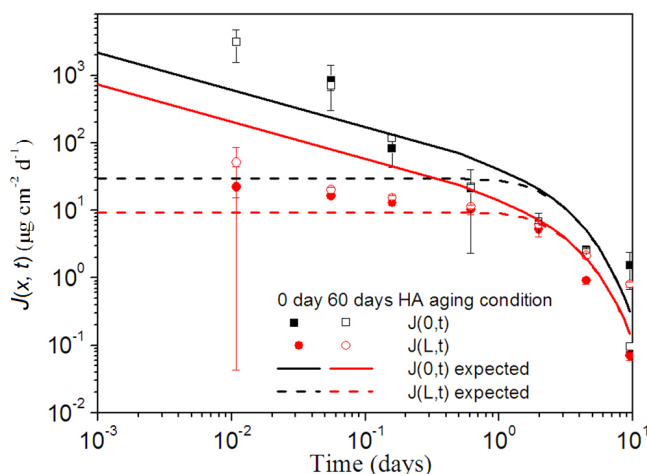


Fig. 3. (Color online) Flux vs. time for  $\text{ReO}_4^-$  by out-diffusion method.

In order to verify the slow reaction kinetics of  $\text{Re(VII)}$  and HA, Fig. 3 shows the out-diffusion results of  $\text{Re(VII)}$  diffusion under aging 0 and 60-day conditions.  $J(L, t)$  was the flux in target reservoir boundary, and  $J(0, t)$  was the flux in source reservoir boundary. The curves were calculated

by using the  $D_e$  and  $\varepsilon_{\text{acc}}$  values obtained from the through-diffusion experiments (Table 2). The data of Re under aging 60-day condition at both boundaries (original target and source reservoir) were in good agreement with the predictions from the through-diffusion experiment, except the first three data points. The dead volume was probably the major factor to enhance the mass of Re, especially in a short time interval (from 30 min to a few hours), to change the reservoirs. In contrast, the  $J(L, t)$  of predicted and measured data is in agreement with each other, however the  $J(0, t)$  were systematically underestimated by the model predictions for the diffusion of  $\text{Re-HA}$  under aging 0 day conditions. This analogue discrepancy at  $J(0, t)$  was in agreement with the  $\text{Cl}^-$  out-diffusion experiment [17, 28, 29].  $J(0, t)$  showed the exponent decreased with time, it can be explained that heterogeneous porosity distributions are of much less importance for through- and out-diffusion at a low concentration boundary. However, they significantly influence out-diffusion results at a high concentration boundary. Fig. 3 also shows that the experimental data was identical under 0 (solid dots) and 60-day (empty dots) conditions. Moreover, the expected curves obtained from aging 60 days provided a better fit than that from aging 0 day. It can be explained that the reaction equilibrium between  $\text{Re(VII)}$  and HA was achieved when the out-diffusion was started under 0 day conditions.

#### IV. CONCLUSION

Diffusion experiments for  $\text{ReO}_4^-$  in the presence of humic acid at different humic acid condition (humic acid equilibrium, aged 0 and aged 60 days) were investigated by using through- and out-diffusion method. Both  $D_e$  and  $\varepsilon_{\text{acc}}$  values were obtained by fitting experimental data using a computer code FDP. The  $D_e$  value of  $\text{Re(VII)}$  under HA aging 60-day condition was larger than that under HA aging 0 day. The experimental data was identical under 0 and 60-day conditions. The results reveal that the interaction between  $\text{Re(VII)}$  and HA is slow. This study implies the importance of further investigation of the  $\text{Tc(VII)}$  and HA interaction should consider the aging time.

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